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# Molten Salt Oxidation: A Thermal Technology for Waste Treatment and Demilitarization

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# Molten Salt Oxidation: A Thermal Technology for Waste Treatment and Demilitarization

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## 1. Abstract

MSO is a good alternative to incineration for the treatment of a variety of organic wastes including obsolete explosives, low-level mixed waste streams, PCB contaminated oils, spent resins and carbon. The Lawrence Livermore National Laboratory (LLNL) has demonstrated the MSO process for the effective destruction of explosives, explosives-contaminated materials, and other wastes on a 1.5 kg/hr bench-scale unit and in an integrated MSO facility capable of treating 8 kg/hr of low-level radioactive mixed wastes. LLNL, under the direction and support of the Joint Demilitarization Technology (JDT) program, is currently building an integrated MSO plant for destroying explosives, explosives-contaminated sludge and explosives-contaminated activated charcoal. In a parallel effort, LLNL also provides technical support to DOE for the implementation of the MSO technology at industrial scale at Richland, Washington.

Over 30 waste streams have been demonstrated with LLNL-built MSO systems. In this paper we will present our latest experimental data, our operational experience with MSO and also discuss its process capabilities .

## 2. Introduction

MSO is a promising alternative to incineration for the treatment of a variety of organic wastes. Lawrence Livermore National Laboratory (LLNL) has prepared a facility in which an integrated pilot-scale MSO treatment system is being tested and demonstrated. The system consists of a MSO vessel with a dedicated off-gas treatment system, a salt recycle system, feed preparation equipment, and a ceramic final waste forms immobilization system. This integrated system was designed and engineered based on operational experience with an engineering-scale reactor unit and extensive laboratory development on salt recycle and final forms preparation.

The MSO/off-gas system has been operational since December 1997. The salt recycle system and the ceramic final forms immobilization became operational in May 1998. In FY 98, we have tested the MSO facility with various organic feeds, including chlorinated solvents, tributyl phosphate/kerosene, PCB-contaminated waste oils & solvents, booties, plastic pellets, ion exchange resins, activated carbon, radioactive-spiked organics, and well-characterized low-level liquid mixed wastes. MSO is shown to be a versatile technology for hazardous waste treatment and may be a solution to many waste disposal problems in DOE sites. The results of the demonstration conducted in FY 98 have been reported [1].

In FY 99 (October 1998 to April 1999) we conducted further testing in the MSO/off-gas system with ion exchange resins, two real waste specimens, activated carbon, and TNT-loaded activated carbon, both at regular feed rates and higher feed rates up to superficial gas velocity of 1.75 ft/s. We also drained the salt three times (SR7, SR8, SR9) in FY 99

and sent the spent salts to the salt recycle system for further processing. This paper describes some of the results obtained from the demonstration of the MSO/off-gas system and the salt recycle system from October 1998 to April 1999.

## 3. Process Description

MSO is a robust thermal treatment process for destroying organic waste. In this process, organic -containing wastes are injected with a stoichiometric excess of oxidant air under a pool of molten carbonate salts at temperatures between 700–950°C. Flameless oxidation takes place within the salt bath converting the organic components of the waste into $CO_2$, $N_2$, and water. The product off-gas leaving the processor is treated to remove any entrained salt particulate and essentially all water vapor before being discharged to the facility off-gas system. Halogens and heteroatoms such as sulfur are converted into acid gases, which are then "scrubbed" and trapped in the salt in forms such as NaCl and $Na_2SO_4$. Using sodium carbonate in the processor, this process occurs according to the reaction shown in Equations 1, 2, 3, and 4, where X represents generic halogens.

$$2C_aH_b + (2a+b/2)O_2 \text{ ----> } 2aCO_2 + bH_2O \quad (1)$$

For nitrogen -bearing organic wastes,

$$C_aH_bN_c + O_2 \text{ ----> } CO_2 + H_2O + N_2 + NO_x \quad (2)$$

For halogenated organic wastes,

$$C_aH_bX_c + c/2Na_2CO_3 + (a+(b-c)/4)O_2 \text{ ----> } (a+c/2)CO_2 + b/2H_2O + cNaX \quad (3)$$

For sulfur-containing organic wastes,

$$C_aH_bS_c + cNa_2CO_3 + (a+b/4+3c/2)O_2 \text{ ----> } (a+c)CO_2 + b/2H_2O + cNa_2SO_4 \quad (4)$$

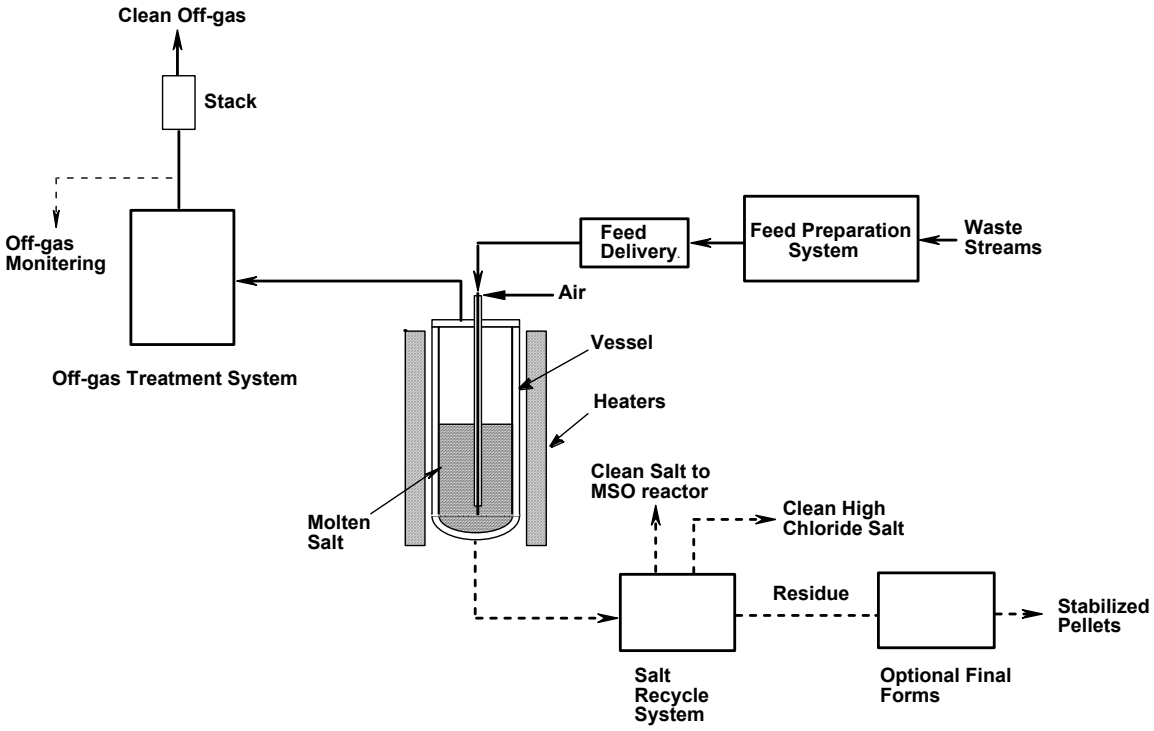
Other non-oxidizable inorganic constituents, heavy metals, and radionuclides are held captive in the salt, either as metals or oxides, and are easily separated for disposal.

MSO has several unique characteristics. The large thermal mass of the molten salt provides a stable heat-transfer medium that resists thermal surges and ensures temperature uniformity and is therefore able to tolerate rapid process fluctuations. Flame-outs are completely avoided, since MSO is a non-flame process that proceeds by catalytic liquid-phase oxidation reactions. Operation of the MSO system is at temperatures hundreds of degrees lower than flame combustion temperatures, which, among other things, minimizes emissions of the radioactive materials from mixed wastes. Acid gases are "scrubbed" by the alkali salts, eliminating the need for a wet off-gas scrubbing system.

## 4. System Description

The integrated MSO system, shown in Fig. 1, consists of several subsystems. It includes a reaction vessel, an off-gas treatment system, a salt recycle system, feed preparation equipment, as well as ceramic final waste forms immobilization system. The waste is fed to the reaction vessel along with oxidant air using a top-feed injection system designed for solid and liquid waste streams at throughputs up to 8 kg/hr for chlorinated solvents, 15 kg/hr TNT slurry, or 10 kg/hr spent carbon slurry. Product off-gas exiting the vessel is then treated in the off-gas system to remove entrained salt particulate, and traces of gas species such as CO and $NO_x$, As waste is injected into the MSO vessel, residues of inorganic components build up in the salt bed which necessitates periodic removal of salt and replenishment with fresh salt to maintain process efficiency. Because many of the metals and/or radionuclides captured in the salt are hazardous and/or radioactive, without further treatment the removed spent salt would create a large secondary waste stream. A salt recycle system is needed to segregate these materials to minimize the amount of secondary waste, and to reduce the consumption of fresh salt [2]. The segregated inorganic residues are then immobilized as a ceramic final form for disposal.

**FIgure 1. Integrated MSO System Diagram**




5. Experiments in the MSO/off-gas System and Results

5.1. Schedule

Several demonstrations were conducted in the MSO/off-gas system with ion exchange resins in October and November 1998, for treatability study with real waste specimens in

January and February, with activated carbon and TNT-loaded activated carbon in March and April 1999. The facility was then orderly shut down and cleaned in May 1999 for the preparation of transfer to a mixed waste treatment facility owned by ATG, Inc. in Richland, Washington near DOE Hanford site. The operational schedule of the integrated facility in FY 99 is shown in Table 1.

Table 1: Operational Schedule of the MSO facility in the Fiscal 1999

| Month | Activity |
|---|---|
| October | Feed system modification for ion exchange resin slurry |
| November | MSO demo with ion exchange resin slurry |
| December | Inspection and calibration of the MSO/off-gas system |
| January | 1st Treatability with real waste specimen, RTS#3 |
| February | 2nd Treatability study with real waste specimen, RTS#4 |
| March | MSO demo with activated carbon |
| April | MSO demo with TNT-loaded activated carbon |
| May | Shut down and cleaned |

MSO demonstration results with plastic pellets, shredded booties, ion exchange resins, and activated carbon have been reported elsewhere [3]. This paper will present the results with TNT-loaded activated carbon and two legacy radioactive waste streams at LLNL.

## 5.2. FY 99 Treatability Study (RTS#3, RTS#4)

### 5.2.1 Description

One of main purposes for conducting the treatability study in FY 99 with real waste streams was to determine the highest superficial gas velocity in order to increase throughput of the MSO vessel. Two real waste specimens were chosen for the MSO treatability study in FY 99. These specimens were received from the Hazardous Waste Management Division at LLNL (waste stream numbers LL-W008 and LL-W016). The first specimen (RTS #3) was PCB-contaminated liquid wastes and the second specimen was chlorinated solvents. Both specimens contain traces of metals and low-level of radionuclides such as tritium and gross alpha and gross beta. Table 2 shows the composition of these two specimens.

**Table 2**

## Real Test Specimens for MSO Treatability Study in FY 98

| | ***RTS #3 Chlorosolvent*** LL-W016 | ***RTS #4 Chlorosolvent*** LL-W008 |
|---|---|---|
| chloroform (g/L) | 2.81 | 0.1 |
| 1,1-dichloroethane (g/L) | 7.09 | 0.5 |
| 1,2-dichloroethane (g/L) | 3.0 | 0.5 |
| 1,1-dichloroethene (g/L) | ND | 20 |
| dichloromethane (g/L) | ND | 1.4 |
| Benzene | 9.05 | ND |
| Xylene | 11.6 | ND |
| 2-butanone | 12.3 | ND |
| Ethyl benzene | 3.4 | ND |
| tetrachloroethane (g/L) | | 40 |
| toluene (g/L) | 25.4 | 0.1 |
| Methylene chloride | 16.5 | ND |
| trichloroethene (g/L) | 1.41 | 10 |
| 1,1,2-trichloro, 1,2,2 trifluoroethane (g/l) | ND | 28 |
| methylchloroform (g/L) | 219 | 1226 |
| Sb (mg/L) | NA | 0 |
| Ba (mg/L) | NA | 1.5 |
| Be (mg/L) | NA | 8.2 |
| Cd (mg/L) | NA | 0 |
| Cr (mg/L) | NA | 1.3 |
| Co (mg/L) | NA | 0.2 |
| Cu (mg/L) | NA | 11 |
| Pb (mg/L) | NA | 11 |
| Mo (mg/L) | NA | 2.5 |
| Ni (mg/L) | NA | 2 |
| K (mg/L) | NA | 4 |
| Ag (mg/L) | NA | 0.3 |
| U (mg/L) | NA | 20 |
| V (mg/L) | NA | 3.1 |
| Zn (mg/L) | NA | 5.3 |
| Hg (mg/L) | Na | 0.04 |
| hydraulic oil, (g/L) | balance | None |
| PCB, mg/L | 61 | None |
| | | |
| Gross Alpha (nCi/L) | 7.26 | 7.26 |
| Gross Beta (nCi/L) | 11.4 | 11.4 |

| | | |
|---|---|---|
| (Tritium (nCi/L)) | 33.1 | 33.1 |

5.2.2. Results of MSO Demonstration with RTS#3 (LL-W016)

Five gallons of RTS#3 specimen was received from HWM in early January. Toluene was then added to the feed container under mixing to prevent phase separation during the feed to the MSO vessel. The demonstration was conducted at superficial gas velocities as high as 1.5 ft/s at 930 C and 950 C, respectively. 20% excess air was used for the oxidation to avoid excessive pressure drops across the GSS filter. Lower temperature (930 C) reduces the salt vapor carryover to the off-gas system but may decrease the destruction efficiency. Off-gas was monitored continuously by off-gas analyzers installed in the off-gas system during the course of the demonstration. In addition to the continuous off-gas monitoring, several gas samples were collected and sent for analysis. Table 3 and table 4 show the run conditions and the off-gas compositions, respectively.

Table 3: Run Conditions for MSO Demo with RTS#3

| No. | Feeds | Superficial gas velocity | Run Conditions |
|---|---|---|---|
| 3A | RTS#3/Toluene | 1.0 ft/s | 950˚C, 1.44 kg/hr, 20% excess air |
| 3B | RTS#3/Toluene | 1.5 ft/s | 950˚C, 2.16 kg/hr, 20% excess air |
| 3C | RTS#3/Toluene | 1.5 ft/s | 930˚C, 2.10 kg/hr, 20% excess air |
| 3D | RTS#3/Toluene | 1.0 ft/s | 930˚C, 1.44 kg/hr, 20% excess air |

Table 4: Off-gas Composition for the MSO Demo with RTS#3

| | Run Numbers | | | |
|---|---|---|---|---|
| Off-gas Species | 3A | 3B | 3C | 3D |
| $CO_2$, % | 9.73 | 9.60 | 10.08 | 9.46 |
| $O_2$, % | 8.06 | 7.26 | 9.82 | 8.01 |
| CO, ppm | 9.9 | 14.5 | 11.7 | 14.0 |
| $NO_x$, ppm | 113 | 97.7 | 110.5 | 100.5 |
| THC, ppm | 0.29 | 0.62 | 0.0* | 0.0* |

*The off-gas analyzers drifted down during the course of the run.

Table 4 shows that off-gas quality was very good with less than 15 ppm of CO and less than 120 ppm of $NO_x$ leaving the MSO vessel, respectively. It also indicates that operating at the higher flow gas velocity of 1.5 ft/s and lower temperature (930 C) would not adversely affect the off-gas quality . CO and $NO_x$ levels in the off-gas were further reduced in the catalytic converter. The concentrations of POHCs (principle organic hazardous compounds), dioxins, and in the off-gas were not detectable [4].

5.2.3. Results of MSO Demonstration with RTS#4 (LL-W008)

10 gallons of RTS#4 specimen was received from HWM in early January. There were two liquid phases in the containers. The top layer (15 wt%) contained mostly water and the bottom layer (85wt%) contained chlorinated solvents and small amount of sludge. The demonstration was conducted at superficial gas velocities as high as 1.5 ft/s at 930 C. 30% and 20% excess air were used for the oxidation to avoid excessive pressure drops across the GSS filter. Lower temperature (930 C) reduces the salt vapor carryover to the off-gas system but may decrease the destruction efficiency. Off-gas was monitored continuously by off-gas analyzers installed in the off-gas system during the course of the demonstration. In addition to the continuous off-gas monitoring, several gas samples were collected during the course of the demonstration and sent for analysis. Table 5 and table 6 show the run conditions and the off-gas compositions, respectively.

Table 5: Run Conditions for MSO Demo with RTS#4

| No. | Feeds | Superficial gas velocity | Run Conditions |
|---|---|---|---|
| 4A | RTS#4,bottom layer | 1.0 ft/s | 930˚C, 5.1 kg/hr, 30% excess air |
| 4B | RTS#4, bottom layer | 1.5 ft/s | 930˚C, 7.8 kg/hr, 30% excess air |
| 4C | RTS#4, bottom layer | 1.4 ft/s | 930˚C, 7.8 kg/hr, 20% excess air |

Table 6: Off-gas Composition for the MSO Demo with RTS#4

| | Run Numbers | | |
|---|---|---|---|
| Off-gas Species | 4A | 4B | 4C |
| $CO_2$, % | 14.9 | 15.6 | 18.3 |
| $O_2$, % | 9.0 | 8.5 | 6.7 |
| CO, ppm | 14.3 | 8.2 | 9.8 |

| | | | |
|---|---|---|---|
| $NO_x$, ppm | 169 | 209 | 212 |
| THC, ppm | 0.34 | 0.0* | 0.0* |

*The off-gas analyzers drifted down during the course of the run.

Table 6 shows that off-gas quality was very good with less than 15 ppm of CO and less than 220 ppm of $NO_x$ leaving the MSO vessel, respectively. It also indicates that operating at the higher flow gas velocity of 1.5 ft/s and lower temperature (930 C) would not adversely affect the off-gas quality. CO and $NO_x$ levels in the off-gas were further reduced in the catalytic converter. The concentrations of POHCs (principle organic hazardous compounds), dioxins, and in the off-gas were not detectable [4].

## 5.3 Demonstration with TNT-loaded Activated Carbon

Demonstration with TNT (trinitrotoluene) -loaded carbon was conducted in April 1999 in an effort to simulate a real waste stream from a demilitarization plant. Table 7 shows the run conditions.

Table 7: Run Conditions for MSO Demo with TNT-loaded Carbon (0.5 wt.% TNT)

| No. | Feeds | Superficial gas velocity | Run Conditions |
|---|---|---|---|
| 1 | 20-40 mesh carbon | 1.0 ft/s | 950˚C, 1.4 kg/hr, 30% excess air |
| 2 | 20-40 mesh carbon | 1.4 ft/s | 950˚C, 2.0 kg/hr, 30% excess air |

A vibratory solid feeder was used to deliver an average feed rate of 1.4 kg/hr and 2.0 kg/hr of 20 to 40 mesh activated carbon loaded with 0.5 wt.% TNT along with excess of oxidant air into the MSO vessel. Molten salt samples were taken before the feed, during the feed began, end of the feed, during the air purge, respectively. These salt samples were sent for analysis. Off-gas quality was monitored by off-gas analyzers during the course of the demonstration. Off-gas samples were also collected and sent for analysis of TNT. Table 8 shows that off-gas composition at steady state for runs 1 and 2. Although the high CO concentration in the off-gas for run 2 was observed, it can be further reduced to ppm level in the catalytic converter. Both NOx and THC levels were very low. TNT in the off-gas was not detectable, an indication of good process efficiency. Analysis of the salt sample show that background ash and carbon content in the melt were negligible.

Table 8: Off-gas Composition for the MSO Demo with TNT-loaded Carbon

| | Run Numbers | |
|---|---|---|
| Off-gas Species | 1 | 2 |
| $CO_2$, % | 11.8 | 15.8 |
| $O_2$, % | 9.3 | 5.8 |
| CO, ppm | 36.1 | 340 |
| $NO_x$, ppm | 6.8 | 19.0 |
| THC, ppm | 0.09 | 0.0* |

*The off-gas analyzers drifted down during the course of the run.

5.4 Results of Demonstration with Fine Carbon Slurry

Demonstration with fine carbon slurry was conducted in April 1999. The purpose of the carbon slurry testing was to determine the efficacy of MSO technology for treating carbon sludge generated in industry and demilitarization plants. The slurry consisted of carbon (100 mesh and finer) and water. It was pumpable at 20 wt% of carbon loading. Table 9 shows the run conditions.

Table 9: Run Conditions for MSO Demo with Fine Carbon Slurry

| No. | Feeds | Run Conditions |
|---|---|---|
| 1 | 100 mesh minus<br>15 wt.% C, 85% H2O | 950˚C, 3.3 kg/hr, excess air |
| 2 | 100 mesh minus<br>20 wt.% C, 80% H2O | 950˚C, 3.3 kg/hr, excess air |

The carbon slurry was pumped to the MSO vessel with excess of oxidant air. The salt temperature was controlled at 950 C and the off-gas composition was monitored by off-gas analyzers during the course of the demonstration. Table 10 shows that off-gas composition at steady state for runs 1 and 2. Excellent off-gas quality was observed. The results show that the carbon slurry/sludge can be effectively treated with the MSO process.

Table 10: Off-gas Composition for the MSO Demo with Fine Carbon Slurry

| | Run Numbers | |
|---|---|---|
| Off-gas Species | 1 | 2 |
| $CO_2$, % | 7.9 | 9.3 |
| $O_2$, % | 13.4 | 12.2 |
| CO, ppm | 8.2 | 6.8 |
| $NO_x$, ppm | 3.3 | 3.0 |
| THC, ppm | 0.2 | 0.04 |

6. MSO Vessel Wall Thickness

The MSO vessel with a 0.5 inches wall was designed to operate to last for 10,000 hours of continuous operation at temperature above 900 C. Since May of 1997, the vessel has

been inspected three times. The vessel was inspected with an ultrasonic meter at various locations along the vessel wall. Results of the inspection are shown in Table 11.

Table 11: MSO Vessel Inspection Results

| Time | Vessel wall thickness Inches | Hours of operation | Corrosion rate inches/100 hrs | Note |
|---|---|---|---|---|
| May, 1997 | 0.500 | 0 | N/A | New Vessel |
| March, 1998 | 0.496 | 150 | 0.0027 | |
| November, 1998 | 0.492 | 750 | 0.0011 | |

Table 11 shows that the corrosion rate was only 0.0027 inches per 100 hours of operation at temperature above 900 degree C in the beginning and corrosion rate dropped to 0.0011 inches/100 hrs. The reduction in corrosion rate was probably due to the formation of protective layer on the inner wall of the MSO vessel At his corrosion rate, the MSO vessel with a 1/2 inch thick wall would be able to operate for 25000 hours. For a MSO treatment plant operating at 5000 hours a year, the MSO vessel would last for 5 years before a replacement vessel is needed.

7. Conclusion

An integrated MSO pilot-scale facility has been built and demonstrations conducted since December 1997. The facility has been demonstrated with over 30 different feeds, including surrogates and real waste streams, liquid and solid. For radioactive chlorinated solvents, as high as 8.0 kg/hr of RTS#4 (a real waste specimen) was fed into the MSO vessel and treated. For TNT-coated activated carbon sized 20 to 40 meshes and smaller, the process efficiency was very good. The MSO technology is mature and can be fielded and implemented in DOE sites, DOD installations, and in some commercial applications.

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